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The Effect of Hydrochloric Acid Pretreatments on 440C Steel Surface Composition and the Adhesion and Endurance of Sputter-Deposited MoS_2 Solid Lubricant Films

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Mechanics and Materials Technology Center
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19 April 1991

Prepared for

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ABSTRACT

The effects of substrate pretreatment on substrate surface chemistry and on film-substrate adhesion, and film endurance (wear life) of sputter-deposited molybdenum disulfide (MoS_2) on 440C bearing steel were investigated. Specifically, 20% hydrochloric acid/ethanol mixtures were used to etch the steel surface prior to deposition or X-ray photoelectron spectroscopy (XPS). Acid etching inhibited fractures at the film-substrate interface generated by brale indentation testing. XPS indicated that the acid etching removed an iron-rich oxide surface layer, exposing a chromium-rich oxide underlayer on the steel matrix. Acid etching did not significantly affect thrust-washer sliding wear life.

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I. INTRODUCTION

Molybdenum disulfide (MoS_2) is a useful solid lubricant for space applications because of its low friction, negligible vapor pressure, and tribological insensitivity to temperature (relative to liquid lubricants). Sputter deposition is a useful process for applying MoS_2 onto component surfaces; the process creates a uniformly thick coating and avoids the use of organic binders, which can outgas in the vacuum of space. MoS_2 is routinely used in release mechanisms and on sliding electrical contacts. There is also a growing interest in using MoS_2 in precision bearings.[1,2] Recently, there has been a significant effort to better understand the relationship between film processing conditions and resultant film structure and composition (both film and interfacial), properties which, in turn, affect tribological performance.[3-6]

Studies indicate that when the lubrication ability of sputter-deposited MoS_2 is assessed, both the as-deposited and deformed microstructures must be considered.[7] As an example, high porosity in the film can lead to large-scale grain fracture near the interface early in wear. The fractured grains become loose debris that can still lubricate in applications where debris is retained, e.g., a telescoping mechanism. A low porosity film can have deformation confined to a surface region and can minimize film debris generation.[7,8] The deformation causes crystal reorientation or crystallization to occur (the particular response being dependent upon initial film crystallinity) such that basal planes align parallel to the surface, facilitating lubrication. Thus, different microstructures with variable porosity can sometimes be acceptable. However, for applications where debris is quickly ejected, e.g., ball bearings, good film-substrate adhesion and low film porosity are required (desirable).[7,9]

Previously, we have shown that brale indentation of sputter-deposited MoS_2 coatings on 440C steel induces film delamination around the crater rim.[8,10] The extent of delamination is affected by indentation load, film morphology and thickness, film-substrate interfacial fracture toughness, and therefore film-substrate adhesion. By plotting delamination length, a, versus

load, L, interfacial fracture toughness, K (which is inversely related to the slope da/dL), can be assessed. For sputter-deposited MoS_2 on 440C steel, da/dL was found to be relatively insensitive to film thickness, while da/dL was noticeably sensitive to morphology. Films with a porous, zone 2 (Thornton model[11]) columnar-plate morphology had a higher fracture toughness than denser, zone 1 films.[8] For particular film morphologies and film preparation conditions, delamination length was found to increase with film thickness and indentation load, in agreement with studies of hard coatings. Indentation tests executed on films of fixed thickness and morphology, but with variable substrate pretreatment, have provided information on the effect of such pretreatment on fracture toughness. Sputter-etch cleaning of the steel substrate prior to deposition, which is a common industrial practice to improve film adhesion, did indeed inhibit indentation-induced delamination of MoS_2 films on 440C steel.

In the previous study,[8] the chemical effects of pretreatment on the steel surface, i.e., changes in surface composition, were not specifically investigated. Besides ion bombardment, acid exposure to the steel surface can also cause etching. Chemical pretreatments are often used in industrial practice to improve generic coating adhesion. In this report, we discuss the effects of hydrochloric acid pretreatments on 440C steel and on the indentation delamination of MoS_2 films subsequently sputter deposited onto the etched surfaces. X-ray photoelectron spectroscopy (XPS) data are presented that identify the compositional changes that occur on the steel surface during chemical and ion etching. Sliding wear endurance as a function of pretreatment is also reported.

II. EXPERIMENTAL

The MoS_2 films were prepared by radio frequency (rf) sputtering, using a chamber described previously.[12,13] The films were sputtered at 2.66 Pa onto 440C steel surfaces (10 × 25 mm) that typically reached 70°C ambient temperature (AT) upon completion of the sputtering process. The conditions produce a zone 2 columnar-plate morphology having a (100) edge-plane orientation parallel to the steel interface with some (110) edge-plane orientation. This microstructure was confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), using procedures described previously.[12,13] Film thickness was about 1250 nm, as measured by profilometry.

Chemical etching was done using 20% HCl in ethanol. The 440C specimens were previously polished to 300 nm grit; the steel Rockwell hardness was 58-60C. All samples were ultrasonically cleaned for 10 min in ethanol. The samples were then exposed to acid for one of the following times: 0 (no exposure, ethanol rinse only); 10, 30, or 60 sec. As will be discussed, ultrasonic agitation was adopted during acid exposure. Following acid exposure, the samples were rinsed in three successive beakers of ethanol for a total of less than 2 min. The samples were then placed in the deposition chamber. All procedures were conducted in laboratory air. The maximum time between pretreatment and initial evacuation was less than 10 min. The variably etched samples were all coated in the same deposition session. Identical procedures were subsequently used to prepare steel surfaces for XPS analysis (as described later). Surface roughness after etching was assessed by profilometry for some uncoated samples.

The films were indented with a Rockwell "C" diamond brale stylus. Indentations were made at various loads that range in discrete steps from 60 to 150 kg. Crack growth as a function of load was later measured by scanning electron microscopy (SEM), following the approach reported previously.[8,10] However, most indentations were performed at 150 kg, and the nature and extent of delamination as a function of acid exposure was assessed.

XPS was performed with a Surface Science Instruments SSX-100 spectrometer using procedures described previously.[14] The unetched and acid-etched steel surfaces were analyzed by XPS as received and later after sputter-depth profiling, to determine the nature of the near-surface region as a function of depth. Argon ions were generated with a sputtering gun using a beam voltage of 2 keV.

Sliding wear tests were performed on a thrust-washer apparatus under conditions described previously.[12] The machine consists of a polished, uncoated 440C disk that slides against a coated steel flat under low loads (3.18 kg dead weight) at a mean sliding velocity of 33 mm sec. The apparent contact area between the rider and the stationary member was approximately 45.2 mm^2. Films were generally run until they failed (arbitrarily defined as that point where the reaction torque exceeded 0.07 N-m).

III. RESULTS

SEM analysis of brale indentations revealed that acid etching did inhibit MoS_2 film delamination (Figure 1). Increasing exposure time progressively reduced film delamination (Figure 2), though the difference between 30 and 60 sec is less than the difference between shorter exposures. Initially, hydrochloric acid ethanol pretreatments were applied with cotton swabs, followed by ethanol rinsing. However, the steel surface visually appeared to be unevenly etched. After MoS_2 deposition onto these samples, brale indentation of different areas on the same sample revealed nonuniform delamination, which correlated to the different visual regions. It was found that placing the samples in a beaker of acid solution during ultrasonic agitation provided a more uniform etch, both in visual appearance and in subsequent brale indentation fracture behavior. Even in the rinsed samples, indentation near the edge of a sample would sometimes cause the sample to tilt during loading. This misalignment resulted in a nonuniform stress distribution around the rim, which led to highly irregular delamination. Therefore, it is recommended that indentation at a given load be done at a minimum of three different areas of a sample, to evaluate the presence of nonuniform interfacial chemistry and or the occurrence of irregular loading. All the delamination data reported here had three to five indentations per load (Figure 3).

Closer examination of the indentation rims (Figure 2) reveals a subtle change in fracture behavior with acid etching. The rinsed sample has extensive film delamination caused by lateral fracture along the steel interface. In addition, radial cracking extends further into the remaining film. Film curvature (relative to the interface) is observed in these radial crack areas, suggesting that lateral fracture has occurred underneath the film but that it has not completely detached into isolated debris. Examination of the 10 sec etch sample (Figure 2) shows less delamination and reduced radial cracking. The 30 and 60 sec etch samples have far less delamination than the 10 sec etch sample; large-scale radial cracking is not present in the 30 and 60 sec etch samples. Discontinuous radial microcracking is present in all four samples.

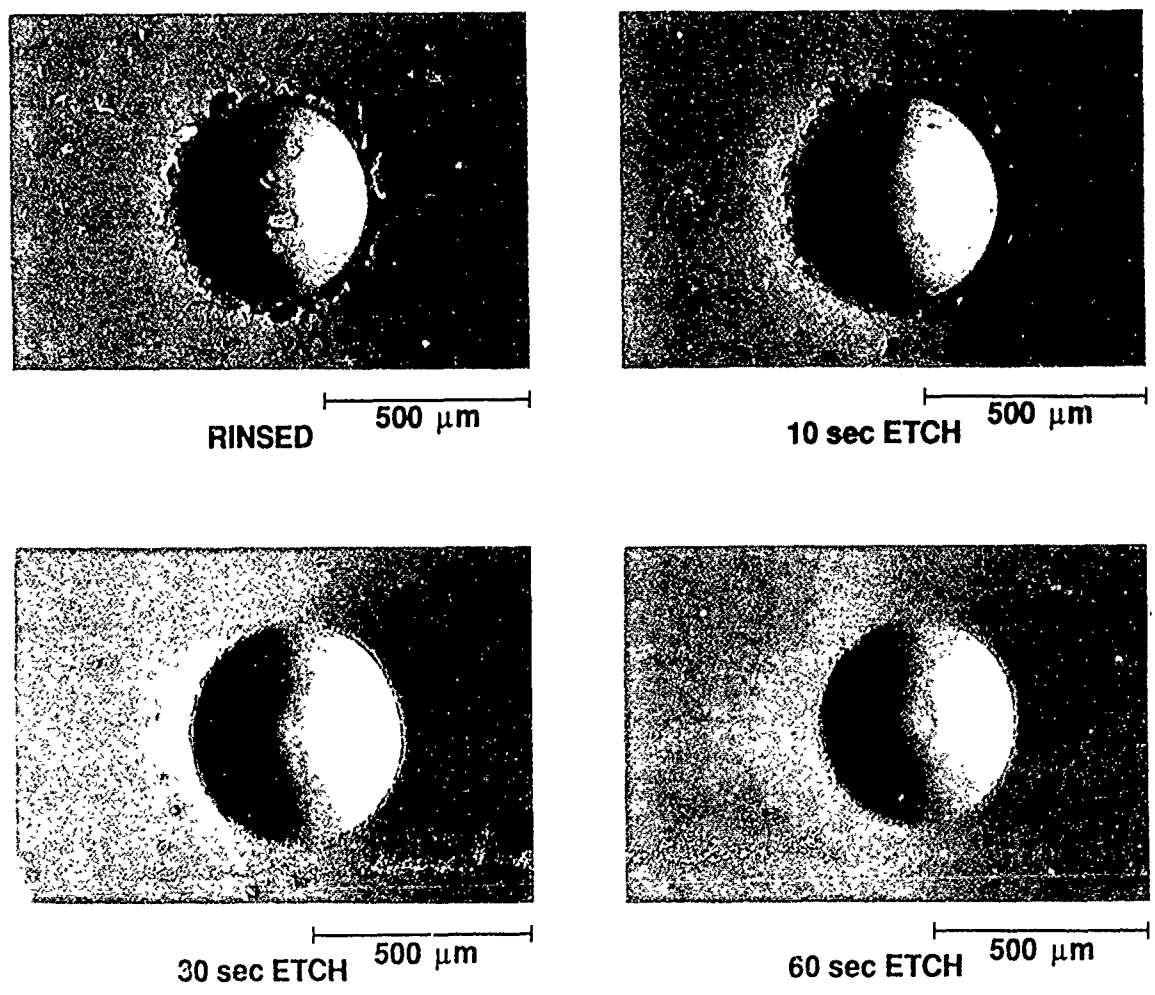

Fig. 1. SEM micrographs of brale indentations on MoS_2-coated 440C steel samples, which had different hydrochloric acid/ethanol etching pretreatment times. Longer exposure time reduces the extent of film delamination, indicating increased film-substrate interfacial adhesion.

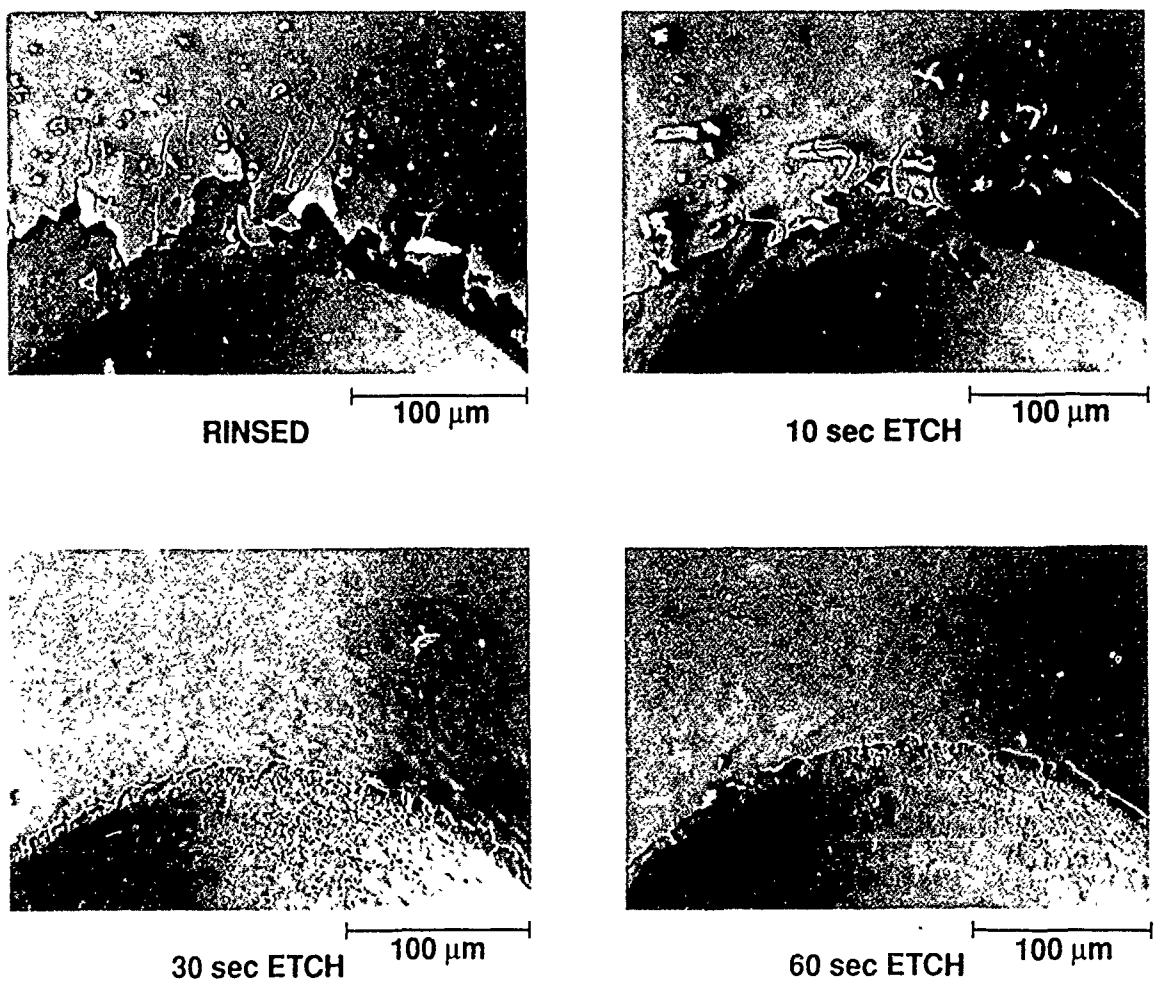

Fig. 2. Closeup of the areas shown in Fig. 1. The rinsed samples have radial cracking beyond the region of film delamination. Etching can reduce the extent of radial cracking (10 sec etch) or eliminate it (30 and 60 sec etches). Localized vertical deformation of the steel is particularly evident in the 30 sec etch sample.

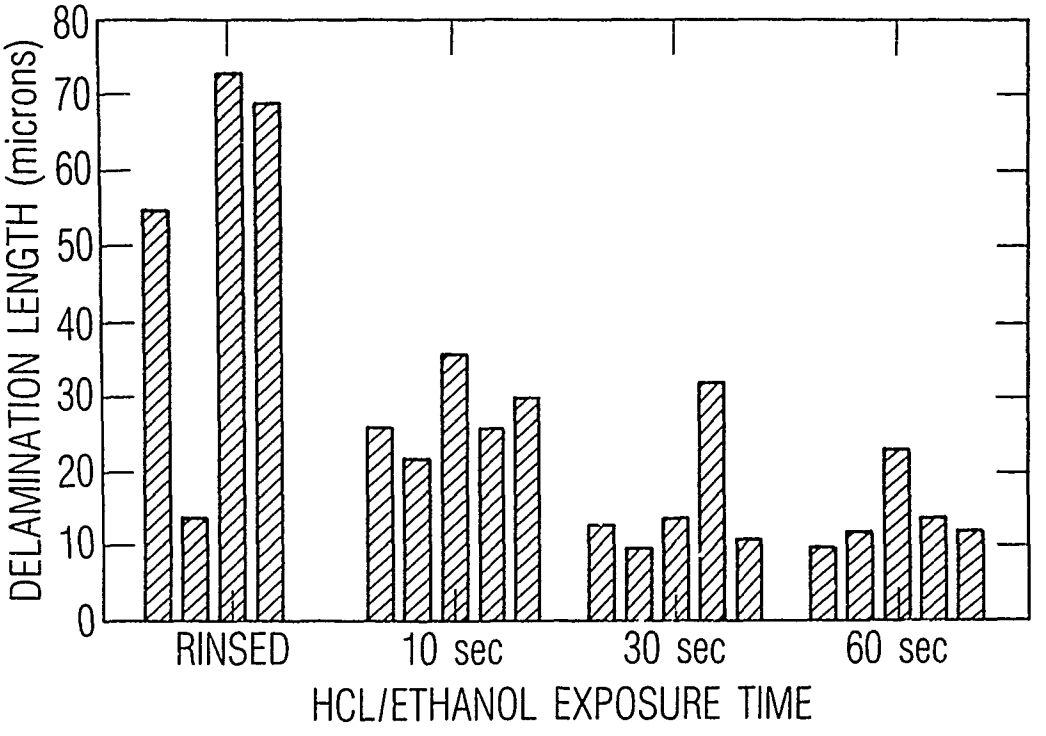

Fig. 3. Film delamination length caused by brale indentation (represented in Figs. 1 and 2) as a function of acid-etching exposure time. Hydrochloric acid/ethanol pretreatment reduces the average delamination length relative to unetched (rinsed) samples.

Such microcracking has been observed before[8] and appears to be initiated by vertical deformation of the steel matrix and carbide fracture in the steel. Vertical deformation is particularly evident in the 30 sec etch sample. Profilometry indicated that the 10 and 30 sec etch samples had an average roughness of 6 nm; the 60 sec etch sample had an average roughness of 17 nm.

XPS studies of the rinsed steel surface region indicated that the composition from surface to bulk consists of (1) a surface contaminant overlayer of hydrocarbon, (2) an iron-rich oxide surface layer, (3) a chromium-rich oxide underlayer, and (4) bulk steel. Figure 4 provides an example of this interpretation, showing the progressive change in Fe and Cr peak intensities from oxide to metal as a function of sputtering time. In Figure 4a, the higher binding energy iron oxide features are removed with sputtering, while the Fe metal peak at lower binding energy grows in intensity. Simultaneously, the intensities of both the chromium oxide and metal peaks increase in intensity (Fig. 4b) while maintaining essentially the same chromium oxide:chromium metal intensity ratio as the iron oxide layer is removed. After the iron oxide layer is sputtered away, the chromium oxide peak intensity falls, indicating that this layer is being sputtered. The steel surface sputtering behavior demonstrates that an iron oxide surface layer covers the chromium oxide underlayer.

This interpretation is consistent with reports in the literature of stainless steels studied with surface analytical techniques.[15-18] The presence of the chromium-rich oxide underlayer is apparently responsible for oxidation passivation of the bulk steel. The iron-rich oxide forms an overlayer for kinetic reasons but structurally does not form a passivated layer.

For the unetched 440C sample, the layer of hydrocarbons present on the surface appears to be 0.5-1 nm thick. This estimate is made from the differences in intensities of the iron and chromium XPS peaks before and after removal of the carbon overlayer. The calculation assumes an exponential peak attenuation dependence on the contaminant layer thickness.

The thicknesses of the oxide layers were estimated from an SiO_2 sputter etch rate of 0.44 nm/min, which should be much more accurate for these species

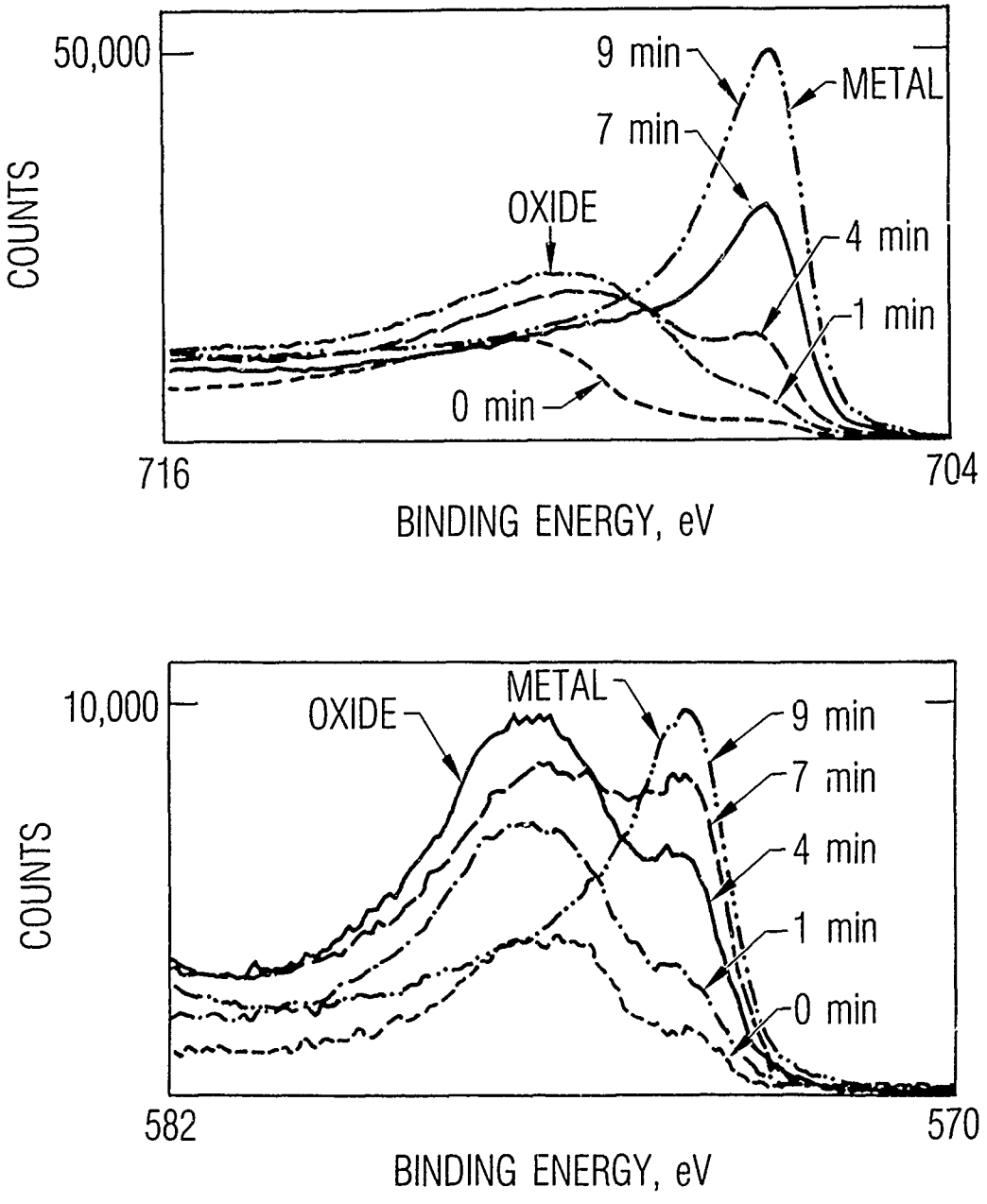

Fig. 4. The (a) Fe $2p_{3/2}$ XPS core level and (b) Cr $3p_{3/2}$ XPS core level as a function of Ar ion sputter time. The sputter times of 0, 1, 4, 7 and 9 min are listed on the respective spectra. The 0 min sputtering spectra for both core levels are significantly smaller than the 1 min sputter spectra due to the presence of the hydrocarbon overlayer.

than for the hydrocarbon layer. The iron oxide layer was virtually gone after 7 min of sputtering, which would give a nominal thickness of ~3.0 nm. The chromium oxide layer, however, began to be sputtered in the sixth minute of sputtering, which indicates that the iron oxide layer is breached in the 6 min time frame, giving perhaps a more accurate thickness of 2.5 ± 0.3 nm. It then took less than 4 min to remove the chromium oxide layer, which gives an approximate thickness of 1.5 ± 0.3 nm.

After the oxide layers have been removed, the steel surface has the following approximate composition: 68% Fe, 18% Cr, 9% C, and 5% O. All of the carbon detected is present as carbide. The 9% C seems quite high for bulk 440C and could indicate that the surface is rich in carbides, even though the Fe:Cr ratio is about right.

The effects of the HCl etches on the iron and chromium core levels are displayed in Figure 5. The intensity of the iron oxide signal is dramatically decreased by the acid etching (Figure 5a), indicating the presence of a much thinner oxide layer than on the unetched surface. The 10 sec etch removed enough of the iron oxide for a 2 min sputter to completely eliminate the remaining layer. This provides us with an upper estimate of 0.9 nm for the thickness of the iron oxide layer remaining after acid etching, assuming that the sputter etch rate of the acid-etched surface is the same. The Cr peaks increase in intensity following the 10 sec etch, but the relative oxide-to-metal peak intensites remain unchanged (Figure 5b). In addition, the chromium oxide feature was also significantly decreased by the 2 min Ar ion sputter. These effects are consistent with the removal of the iron oxide overlayer. The 30 sec etch surface also had much less iron oxide than the unetched surface but appeared to have more surface iron oxide present than the 10 sec etch sample (Figure 5a). This thicker iron oxide layer, however, was also eliminated by only 2 min of sputtering. The Cr 2p XPS peaks obtained after the 30 sec etch were quite similar to the 10 sec etch results. Finally, the surface produced by the 60 sec etch was quite heterogeneous. The Fe 2p spectrum in Figure 5a shows a large amount of oxide, but other portions of the sample had measurably less oxide. The Cr XPS features (Figure 5b) after the 60 sec etch were similar to those obtained after shorter etches. All acid-

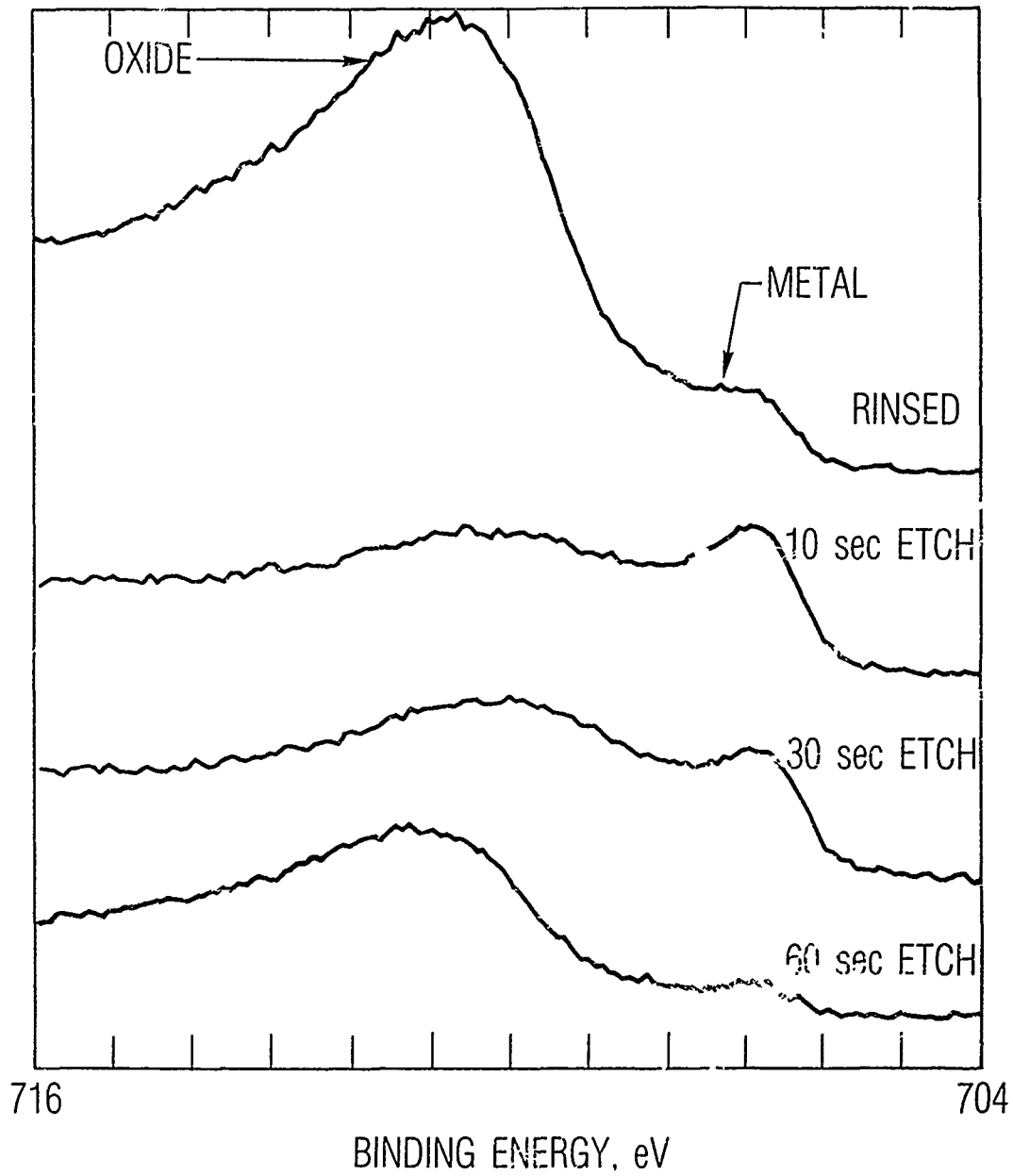

Fig. 5a. The Fe XPS core level as a function of acid etching. From the top of each data set, the spectra are from the unetched (rinsed) surface, the 10, the 30, and the 60 sec hydrochloric acid/ethanol etches.

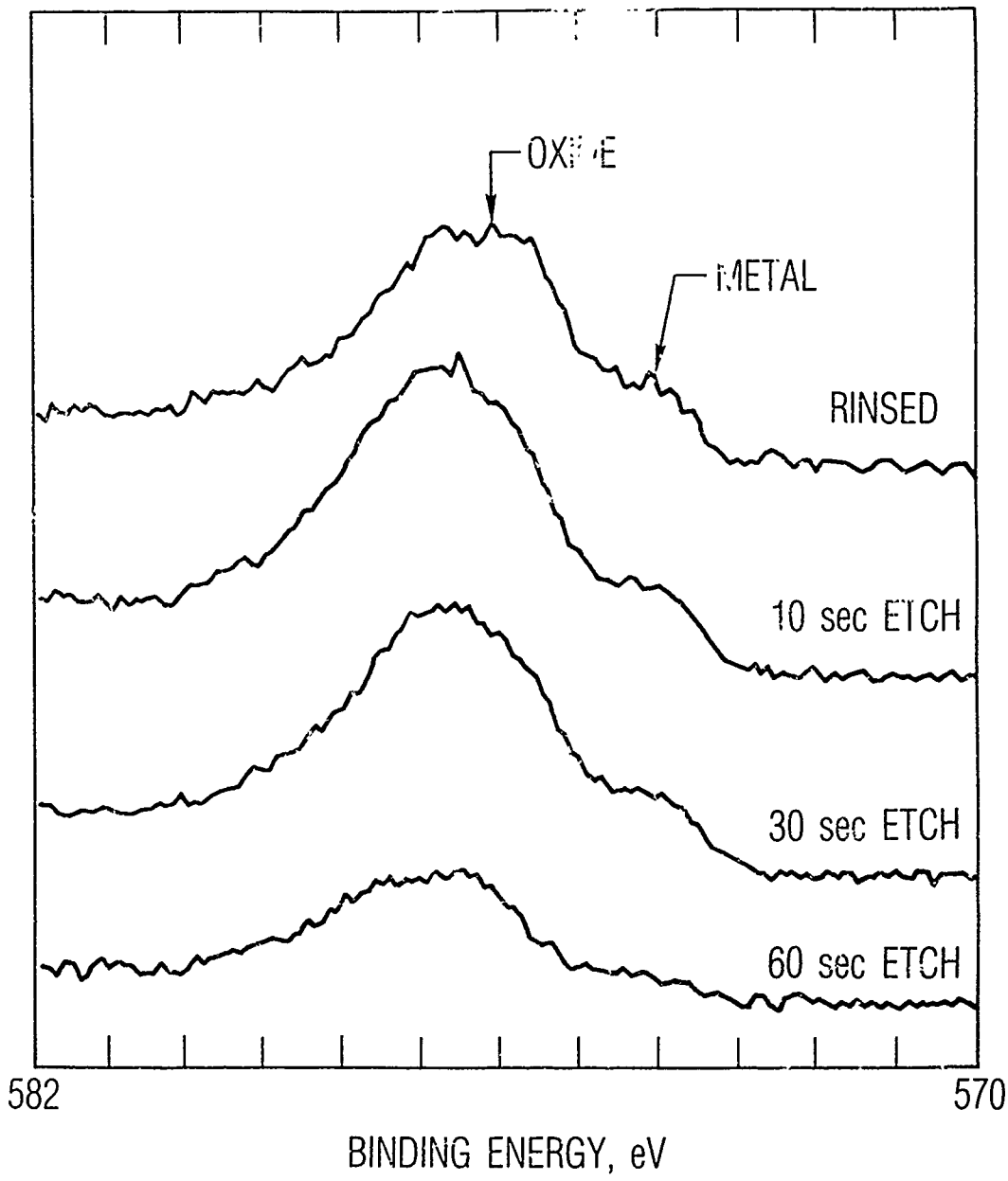

Fig. 5b. The Cr XPS core level as a function of acid etching. From the top of each data set, the spectra are from the unetched (rinsed) surface, the 10, the 30, and the 60 sec hydrochloric acid/ethanol etches.

etched surfaces had large amounts of hydrocarbon contamination, with the contamination seemingly increasing with etch time.

Chlorine was detected on the surfaces of the acid etched samples. Most of the Cl remained on the surface after a brief 20 sec sputter performed to remove the C contamination, indicating that the Cl was interacting with the steel (most likely the surface iron oxide component). The Cl was completely removed after the 2 min sputter, along with the iron oxide.

Sliding wear endurance data as a function of acid etching is shown in Figure 6. Scatter, within lifetime data for a given pretreatment, is evident (see rinsed and 30 sec etch samples). This scatter, along with the limited database, does not reveal a consistent trend of lifetime as a function of etching for this type of tribological contact.

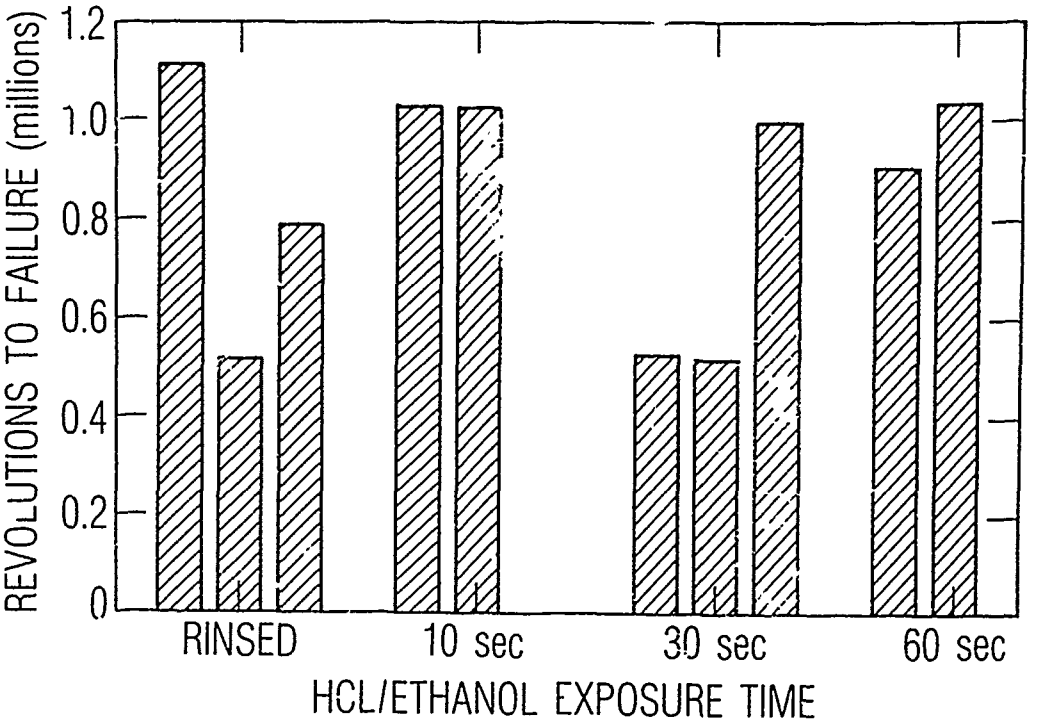

Fig 6. Thrust-washer sliding wear life as a function of hydrochloric acid/ethanol exposure time. No consistent trend is present.

IV. DISCUSSION

The experimental evidence indicates that hydrochloric acid/ethanol pretreatment of 440C bearing steel can improve the fracture toughness of MoS_2 sputter-deposited films on this substrate. The etching can be conducted in air, and the effective surface modification is apparently stable for at least 10 min until deposition chamber pumping is initiated. XPS shows that the HCl removes most of the thin-surface iron-rich oxide. The remaining chromium-rich oxide underlayer, along with deposited chlorine and remnant hydrocarbon, constitutes the new surface upon which deposition then occurs. The CrO_x probably remains because FeO_x is soluble in HCl, while CrO_x is relatively insoluble.[19]

Presputtering before deposition can inhibit indentation delamination even more than the acid etching discussed in this report.[8] The XPS study of the rinsed steel surface shows that the entire Fe-Cr-O layer is quite thin; it is likely removed entirely by ion sputtering pretreatments often used in film deposition. Thus complete removal of the oxide may further improve fracture toughness. Other chemical etches that would remove the CrO_x underlayer could lead to further improvements in adhesion. These stronger etchants might uncontrollably increase surface roughness by rapidly etching the steel matrix without etching adjacent alloy carbides. Such roughness may be unacceptable for precision bearings. The relative insolubility of CrO_x to HCl may make the process a compromise between increasing surface reactivity and cleanliness to improve film adhesion and minimizing substrate surface roughening. However, even prolonged HCL exposure (60 sec etch in this study) caused heterogeneous composition and larger roughness to develop. Future studies should investigate the effects of different acid concentrations.

The interaction of MoS_2 with CrO_x requires further attention. Studies have been reported[20-22] that investigate the chemical interaction of iron evaporated onto molybdenite, followed by high-temperature annealing. The studies have attempted to determine the thermodynamically stable products that form, which might suggest suitable interlayers or pretreatments to improve sputter-deposited MoS_2 film adhesion onto steel. It would be interesting to

investigate Cr and MoS_2 interactions, although the experiments used high temperatures to facilitate reaction kinetics. Such reactions may occur at lower temperatures in sputter-deposited films because the films are highly defective, containing stacking faults, dislocations, and basal-plane curvature, as indicated by transmission electron microscopy (TEM).[6] These defects could act as fast pathways for diffusion.

The substrate surface chemistry can also affect the crystalline orientation of sputter-deposited MoS_2. An active sites model[23] has been proposed in which chemically active sites (either -OH groups[23] and/or carbonaceous groups[14]) on a surface induce edge orientation. Thermal processing on silicon[23] or acid pretreatments on SiC[14] remove these active sites, allowing the thermodynamically favored basal orientation to evolve in thin films. TEM studies of MoS_2 sputter deposited onto amorphous carbon indicate that both basal- and edge-oriented "islands" can be present in the early stages of growth. The mixture of islands has been explained by a revised model that allows a heterogeneous distribution of active sites.[6] However, once edge islands nucleate, the TEM analysis shows that they rapidly grow and shadow continued basal island growth. Acid etching that exposes CrO_x apparently yields or retains active sites that nucleate edge islands. Further analysis is needed to determine if the hydrochloric acid/ethanol etching affects the <u>initial</u> distribution of edge and basal islands at the interface (i.e., < 40 nm thick).

Hydrochloric acid/ethanol etching did not have a clear effect on thrust-washer sliding wear endurance. However, this type of tribological contact may retain loose film debris, in which case adhesion is less critical. Other types of contact in which film debris is quickly ejected, such as rolling element bearings, may be more favorably affected by chemical- or ion-etching pretreatments.

V. CONCLUSIONS

Chemical etching using 20% hydrochloric acid/ethanol was done on 440C bearing steel surfaces prior to MoS_2 sputter deposition and subsequent indentation and wear testing, or prior to XPS analysis. The following conclusions were made.

1. Delamination by indentation was significantly inhibited by acid etching. The chemical pretreatment was effective in laboratory air. However, ion bombardment showed greater improvements to interfacial fracture toughness.

2. The unetched surface consisted of a hydrocarbon overlayer, followed by an iron-rich surface oxide layer, followed by a chromium-rich oxide underlayer, followed by the bulk metal. The chromium-rich layer provides oxidation passivation. The thinness of the oxide layers suggests that they are completely removed during the ion bombardment pretreatments often done before MoS_2 deposition. Thus deposition probably occurs onto a bulk-like steel surface when presputtering is done.

3. Acid etching removed the iron-rich oxide surface layer, leaving the chromium-rich oxide exposed, apparently because this oxide is relatively insoluble in HCl. Hydrocarbons and chlorine were present on the acid-etched surfaces. Although other chemical treatments might remove the CrO_x and possibly improve film adhesion to the level of ion etching, surface roughness might also increase. Surface roughness did increase after the 60 sec etch; surface composition also differed at various areas.

4. Hydrochloric acid ethanol pretreatment of 440C steel did not systematically affect thrust-washer sliding wear endurance. Loose film debris may be retained in this test contact region, in which case adhesion would be less critical.

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